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(21) International Application Number: PCT/EP99/03547 (22) International Filing Date: 24 May 1999 (24.05.99) (30) Priority Data: MI98A001159 26 May 1998 (26.05.98) IT (71) Applicants (for all designated States except US): UNIVERSITA' DI ROMA "TOR VERGATA" [IT/IT]; Dipartimento Di Scienze e Tecnologie Chimiche, Via della Ricerca Scientifica, I-00133 Roma (IT). UNIVERSITA' DEGLI STUDI DI ROMA "LA SAPIENZA" [IT/IT]; Dipartimento Di Energitica, Piazzale Aldo Moro, 05, I-00185 Roma (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): TERRANOVA, Maria, Letizia [IT/IT]; (IT). ROSSI, Marco [IT/IT]; Università degli Studi di Roma "La Sapienza", Via A. Scarpa, 14-16, I-00161 Roma (IT). SESSA, Vito [IT/IT]; (IT). PICCIRILLO, Susanna [IT/IT]; Università di Roma "Tor Vergata", Via della Ricerca Scientifica, I-00133 Roma (IT). (74) Agent: MINOJA, Fabrizio; Bianchetti Bracco Minoja S.r.l., Via Rossini, 8, I-20122 Milano (IT).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: NEW CLASS OF DIAMOND-BASED MATERIALS AND TECHNIQUES FOR THEIR SYNTHESIS		
(57) Abstract <p>Hereafter are described diamond-based composite materials consisting of sub-micrometric or nanometric dispersions of metallic elements semiconductors and their inorganic compounds in diamond-structured carbon polymorphic matrices together with the techniques and apparatus for their preparation.</p>		

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NEW CLASS OF DIAMOND-BASED MATERIALS AND
TECHNIQUES FOR THEIR SYNTHESIS

The present invention refers to diamond-based composite materials,
5 in particular to composite materials consisting of sub-micrometric or
nanometric dispersions of metal elements, semiconductors and inorganic
compounds thereof in diamond-structured carbon polymorphic matrices.

BACKGROUND

Over the last few years, there has been a growing interest in studies
10 concerning carbon-based materials which offer vast exploitation
possibilities in many advanced technological applications. Synthesis of
new structures such as thin diamond films (D), diamond-like (DL), nano-
tubes, intercalated graphite, C-C composites and Fullerenes has posed
unexpected and stimulating scientific problems, and research along these
15 lines will constitute one of the qualifying fields of the science of materials
in the years to come.

The diamond, thanks to its excellent mechanical, thermal, optical,
electric and chemical properties, can be considered not only as a fully
qualified material for technologically advanced applications and
20 competitive when compared to traditional materials, but also in some cases
as the only available option.

Towards the end of the 1970s in the USSR, a group of researchers
developed techniques for the deposition of diamond layers in conditions of
low P/low T ($P < 1$ atm; $T < 1000^{\circ}\text{C}$), and therefore, in the field of the
25 thermodynamic metastability of this phase.

At the beginning of the 1980s, diamond synthesis in the form of thin
layers deposited on various materials by means of activation of gaseous
mixtures, became an important technology which generated an ever-

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growing interest in the scientific community.

At an international level, the leading nations in this sector are the USA and Japan and they can count on industrial groups and research centres all united in a huge financial effort.

5 Compared to the great expectations surrounding a material which combines properties of high thermal conductivity (2000 W/m K), excellent transparency (0.22-2.5 micrometres, > 6 micrometres), high resistance (10^{16} Ohm cm), extreme hardness (90 Gpa) and chemical inertia, the applications which have actually reached the market are still quite limited
10 (X-ray windows, high-frequency acoustic diffuser diaphragms, coating for surgical cutting instruments, inserts for instruments to cut "non-hard" materials, anti-friction coatings, and a few others). (Abstracts from the Convention "DIAMOND '96", Tours, 8-13 Sept. 1996).

A specific sector of diamond research is directed towards diamond
15 doping, creating donor and acceptor centers which, giving rise to type "n" and type "p" electric conductivity respectively, confer characteristics of a "semiconductor" to the diamond. The most commonly used doping agent is B, which is inserted as a substituent into the diamond lattice during the gaseous phase deposition process, or implanted into the already grown
20 film. We have no evidence in scientific literature of processes to insert elements or compounds (ceramics, oxides) in a crystalline diamond matrix and obtain, therefore, mixed phases. Unlike the doping process, in this case we can talk of "dispersions" of the introduced species "among" the grains of the polycrystalline structure of the diamond, not inside the lattice itself.

25 Syntheses of mixed phases have been carried out for DL. For these materials, substantially amorphous or only with a short range structural order, it has been seen that the basic properties may vary depending not only on the ratio $C(sp^2) / C(sp^3)$ and the content in H, but also on the

introduction of metals and/or ceramics into the carbon matrix. Transition metals of the IV-VI groups were inserted into DL structured films (V. F. Dorfman and B. N. Pypkin, Surf. Coat. Technol. 48,193 (1991)). At low concentrations ($< 15\text{-}20$ at. %), the mechanical properties are controlled by the characteristics of the carbon phase. DL structured films containing transition metals possess interesting optical properties (L. Martinu in "High Energy Density Technologies in Materials Science", Kluwer Academic Publ. (Dordrecht, 1990); C. P. Klages, R. Memming, Materials Science Forum 52/53, 609 (1990)) and charge transport and superconductivity properties (A. D. Bozhko, S. M. Chudinov, D. Yu. Rodichev, B. N. Pypkin, S. Stizza, M. Berrettoni and A. Briggs, Phys. Stat. Sol. 177, 475 (1993)). For example, it has been seen that the electric percolation threshold depends largely on the structural characteristics of the metallic dispersions. At high concentrations, the materials acquire considerable anti-wear and anti-friction properties (E. Bergmann, Proc. 2nd Int. Conference on Application of Diamond Films and Related Materials, eds. M. Yoshikawa, M. Murakawa, Y. Tzeng and W. A. Yarborough (MYU, Tokyo 1993) p. 833). Subjected to thermal cycles ($T > 800$ °C), DL films containing Ti have also demonstrated high resistance to graphitization.

State-of-the art and technical problem

A first problem regards the synthesis and utilisation of diamond film. The high number of research studies carried out during the last decade in the field of gaseous phase deposition has led to the development of methodologies which now make it possible to obtain good quality coatings (in terms of area covered, preferential orientation, phase purity, etc.) on many materials. However, some fundamental problems remain unsolved, such as:

- poor adhesion of the diamond films to the substrate materials. Different values of the thermal expansion coefficient and the elastic modulus between diamond and substrate, as in the diamond-substrate lattice mismatch, are responsible for the presence of residual stress and fragile phases in the interfacial area. Especially in the case of thick deposits, these factors lead to a high degree of detachment.

- Deposition of the diamond on so-called "hostile" substrates. (Fe, Co, steel, iron alloys, etc.). As it is known, it is impossible to deposit the diamond directly onto these materials, because of the high diffusion and reactivity of the C-metal system. Generally, this problem is faced by means of pre-treatment of the substrate, especially pre-depositions of amorphous carbon layers. However, the diamond films obtained in this way demonstrate poor adhesion.

- Diamond coating of cutting instruments. The use of this type of coating is limited to the cutting of "non-hard" materials since the overheating provoked by the operation leads to a process of graphitization of the diamond.

Summary of the Invention

It has now been found that diamond-based composite materials consisting of sub-micrometric or nanometric dispersions of metal elements, semiconductors and inorganic compounds thereof in diamond-structured and diamond-like carbon polymorphic matrices make it possible to overcome these known technical problems. Composite materials as now defined are the first object of this invention.

Another object of this invention is a process and the relevant apparatus for the preparation of these materials.

The industrial uses of new composite materials are a further object of this invention

These and other objects shall be described hereunder in detail with the help of examples and drawings.

In particular, the figure illustrates the apparatus for the preparation of the composite materials of this invention. This apparatus was specifically
5 designed for the synthesis of the new materials.

Detailed Description of the Invention

The synthesis technique according to this invention provides the connection of a hot filament (HF) or microwave (MW) CVD (Chemical Vapour Deposition) reactor to a system for controlled introduction of
10 powders and/or volatile precursors, in order to obtain a new class of carbon materials.

The proposed methodology makes it possible to obtain a vast spectrum of diamond-based composite materials consisting of sub-micrometric or nanometric dispersions of metal elements, semiconductors
15 and their inorganic compounds in diamond-structured carbon polymorphic matrices. The materials are deposited in the form of coatings, films and thin layers on suitable substrates.

The composite materials obtained by using this technique as a basis display extremely variable compositions (from only traces to about 100%)
20 and different structures, schematically summarised hereunder:

- nanometric dispersions distributed both homogeneously over the entire thickness and according to gradients of concentration (so pre-announcing themselves as "functionally gradient materials");
- distribution of isolated micrometric clusters, segregated to grain
25 borders or linked in irregular chains.

Regarding the matrix, it is possible to independently modulate its crystallographic characteristics (degree of crystallinity, preferential orientation, phase purity).

Furthermore, considering the variety of the components (metal elements, semiconductors and inorganic compounds thereof) which can be inserted into the diamond matrix, and the possibility to modify the composition of the gaseous phase which acts as precursor, it can be seen
5 how the synthesis methodology described herein is highly versatile and makes it possible to synthesise a vast range of composite materials.

Advantageously, the formation on the substrate surface of a composite layer with concentration gradient containing a dispersion of the same material as the substrate and where the percentage of the diamond
10 phase progressively increases towards the exterior, can effectively contrast the poor adhesion of the diamond film to the substrate, releasing stress and therefore improving adhesion of the coating to the substrate.

Another advantage of the composite materials subject of this invention is the elimination of, or reduction in, the problems related to the
15 diamond-hostile layer interface. In this case too, it is useful to previously deposit composite intermediate layers where the concentration of metal diminishes gradually. In this way, it is possible to modulate the C-metal interaction, so generating an interface which acts as a buffer and makes it possible to obtain a diamond coating effectively anchored to the hostile
20 substrate by a carbide-like layer.

The diamond-matrix layers containing dispersions of some transition metals show a rise in temperature (ΔT) related to the diamond/graphite phase transition. This ΔT may be varied according to the nature and concentration of the inserted metal, and to the degree of carburization
25 reached during the process. This makes it possible to use the composite materials in cutting instruments even in the case of "hard" materials.

It should be noted how the formation of mixed diamond/metal phases does not modify the characteristical properties of the pure diamond in

terms of reduction in friction (anti-wear coating).

By applying the teachings of this invention, it is possible to selectively produce composite layers which, possessing unique characteristics, can satisfy quite complex technological requirements, or,
5 in any case, technological requirements which cannot be satisfied by the use of other materials.

For example, for each type of conducting metal or carbide, the structural characteristics of the dispersions (nano-dispersions, clusters, concatenated clusters) define the charge transport properties, modifying
10 the electric resistivity which goes from values typical of the diamond (approx. 10^{16} Ohm cm) to values typical of a good conductor (10^{-3} - 10^{-6} Ohm cm). This means that diamond-based composite layers can combine the exceptional tribological, mechanical and chemical (high inertia) properties of the diamond with the characteristics of a conductor.

15 This makes it possible to use the diamond film as a membrane for sensors, electrodes, transducers in systems which simultaneously present both chemical (acid and basic reagents, sea-water, biological liquid) and electrochemical (corrosion) aggressiveness, as well as critical mechanical conditions (abrasion, wearing). The resistance of the diamond to high
20 temperatures, together with its capacity to act as a heat sink, also makes it possible to use these devices in surroundings with high temperatures (at least up to approx. 800°C).

Furthermore, electric or micro-electronic devices, which may be discrete, integrated or hybrid, constituted by or including and/or coated
25 with conductive diamond layers, can be used in all those situations where bio-compatibility is required (on-site medical diagnosis, etc.). Moreover, the introduction of metallic elements, semiconductors and their inorganic compounds makes it possible to modulate the electronic affinity of the

diamond-based films. In one particular application of this invention, the composite materials are useful for the coating of metallic prostheses to be planted in the human body, for example the thighbone upper joint, orthopaedic prostheses, orthodontic implants, etc.

5 The introduction of chemical species in a polycrystalline diamond matrix also alters its optical properties. Depending on the nature and concentration of the introduced species, it is possible to modulate the refraction index (value for the diamond: 2.41) and act on the transparency, modifying both the values and the interval (for the diamond: 0.22-2.5
10 micrometres and > 6 micrometres).

For concentrations higher than the percolation threshold, the diamond/metal composite may show characteristics of a superconductor.

Mixed layers containing ions which emit in wavelengths included in IR fields, near IR, UV or visible at room temperature, are promising
15 candidates for use in the solid state laser sector and electro-optical devices.

It should be noted that if the diamond-based deposits are characterised by concentration gradients within the layers, the deposits obtained become "functionally gradient material" (FGM).

The deposition apparatus schematically illustrated in the diagram is of
20 a new conception and has been specifically designed for deposition of carbon-based mixed phases. The configuration given makes it possible to introduce into the synthesis chamber (1), in a controlled and repeatable manner, metal elements, semiconductors and inorganic compounds thereof both in the form of volatile compounds and sub-micrometric powders. The
25 powders (pure elements or compounds) or the volatile compounds are contained in a tank (8) and are transferred to the synthesis chamber by means of a device (2) which includes a system of gas flows (3,5) which makes it possible to control the density of the powders (or vapours) present

in the gas. In particular, the concentration of the particles in the gaseous flow is measured in two areas (separated by a flow measuring and control system), by means of two particle counters (4), based on laser and controlled by computer. By means of specifically designed software, the measurement readings are used to operate the various control valves present. The system ensures control of the quantity of powders (or vapours) introduced into the synthesis chamber, according to a prefixed scheme for each single experiment. The described system is produced in quartz as far as the external part of the chamber is concerned. The part of the system for introduction inside the chamber is in molybdenum. Uniform distribution of metals on the entire carbon-based film deposition area is carried out by means of a particular geometrical configuration of the final part of the introduction system (7), schematically illustrated in the insert to the diagram. The final part of the introduction system is substantially made up of a tube (diameter=8mm), closed at one end and with a row of conical orifices (with dimensions calculated so as to evenly spread the flow over the deposition area), whose axis is parallel to the surface of the substrate where the carbon-based materials are to be synthesised. Another important characteristic is the system to control the temperature of the substrate which includes a suitable heating device, at least one thermocouple and means for temperature control. The growth apparatus described herein makes it possible to control the size of the precipitates and their dispersion in the carbon matrix and, simultaneously, the structure and composition of the carbon phases. By varying the process parameters, it is possible to introduce the metal elements, semiconductors and inorganic compounds thereof into the carbon matrix in the form of isolated nano-clusters or micrometric clusters linked in irregular chains.

The apparatus of this invention, in accordance with the common

knowledge in the art of chemical deposition in the vapour phase (CVD), is provided with all devices and means necessary for this process, such as vacuum devices, sample loading, flow controls, etc.

5 The conditions of the process can be determined by the person skilled in the art, making use of the common knowledge.

In one typical aspect of this invention, the temperature of the substrate during deposition is between 500 and 950°C, the pressure in the cell during deposition is between 30 and 100 torr, the flow of the hydrocarbon/hydrogen mixture in the cell is between 50 and 300 cm³/min; 10 the hydrocarbon/hydrogen ratio in the flow is between 0.5 and 3%; the carrier gas, conventionally chosen among nitrogen and noble gases, is between 10 and 120 cm³/min.

Before introduction into the chamber, the substrates should be preferably treated by means of abrasion with powders and diamond paste 15 and cleaned with mixtures, for example acetone-based, in an ultrasound bath.

In another aspect, the apparatus of this invention can be used for the synthesis of another super-hard carbon material, C₃N₄. The crystalline shape (β-hexagonal) of this material, on the basis of theoretical estimates, 20 should possess mechanical characteristics (approx. 400 Gpa) better than those of the diamond. It should be pointed out that experimental measurements do not exist for a material which, up to now, seems to have been obtained in only a few (and controversial) experiments and, in any case, in quantities which do not allow direct measuring. Utilising flows of 25 N₂ as a carrier gas, deposits were obtained consisting of crystalline grains of C₃N₄ introduced into a diamond matrix.

The following example further illustrates the invention.

EXAMPLE

Using the above-mentioned apparatus, a diamond-based film containing Nd was prepared.

The deposition conditions are the following:

5 Hot filament CVD chamber; temperature of Ta filament (diameter 0.3 mm): 2180°C; filament-substrate distance: 6mm; substrate: Si (100).

Duration of process: 120 min; temperature of the substrate during deposition: 650°C; gaseous mixture: 1% CH₄ in H₂; flow of this mixture: 200 cm³/min (at c.s.); pressure in cell: 36 torr; flow of carrier gas (Ar): 50
10 cm³/min (at c.s.); metal precursor: Nd(III)-acetylacetonate (powder).

The film so obtained was characterised by the following properties:

COMPOSITIONAL carried out by means of XPS (X-ray Photoelectron Spectroscopy): in the spectra appears the characteristic signal of C (1s) and those of the Nd at 979-983 eV (relative to the state 3d
15 (5/2)) and at 1001-1006 (relative to the state 3d (3/2)).

STRUCTURAL carried out by means of RHEED (Reflection High Energy Electron Diffraction): the diffraction patterns reveal the presence of the diamond phase (spatial group Fd3m), in polycrystalline form without the presence of preferential orientation. An analysis of the
20 diffraction signals underlines the presence of other phases consisting of dispersed nano-crystalline grains, identified as Nd and Nd oxides.

MORPHOLOGICAL carried out by means of SEM (Scanning Electron Microscopy): the morphology confirms the structural data obtained with RHEED.

25 ELECTRICAL: measurement of the electrical characteristics, carried out with the Pauw method in the temperature range of 100-500 K, yielded conductivity values between 10⁺² and 10⁺³ (ohm⁻¹ cm⁻¹).

CLAIMS

1. Diamond-based composite materials consisting of sub-micrometric or nanometric dispersions of metal elements, semiconductors and inorganic compounds thereof in diamond-structured carbon polymorphic matrices.
2. Materials according to claim 1, wherein these metal elements, semiconductors and inorganic compounds thereof are present in concentrations varying from traces to approx. 100%.
3. Materials according to claim 1, in the form of nanometric dispersions.
4. Nanometric dispersions according to claim 3, which are homogeneous dispersions.
5. Nanometric dispersions according to claim 3, which are gradient dispersions.
6. Materials according to claim 1, in the form of distribution of isolated micrometric clusters.
7. Materials according to claim 1, in the form of materials segregated to grain borders.
8. Materials according to claim 1, in the form of materials linked in irregular chains.
9. Materials according to any of claims 1 - 8, wherein the crystallographic characteristics of the matrix can be independently modulated.
10. Materials according to claim 1, consisting of a composite layer with gradient concentration containing a dispersion of the same material as the substrate and where the percentage of the diamond phase progressively increases towards the exterior.
11. Apparatus for the preparation of diamond-based materials, in particular according to claims 1-10, which provides the coupling of a hot filament (HF) or microwave (MW) CVD (Chemical Vapour Deposition) reactor

with a system for controlled introduction of powders and/or volatile precursors.

12. An apparatus for the preparation of diamond-based composites, in particular according to claim 11, which includes a synthesis chamber (1),
5 the external part of which is in quartz; at least one device (2) for the introduction of metal elements, semiconductors and inorganic compounds thereof, said device being made of molybdenum and its final part being substantially made up of a tube (6) (diameter = 8 mm), closed at one end and with a row of conical orifices (7) with dimensions calculated so as to
10 evenly spread the flow over the deposition area, whose axis is parallel to the surface of the substrate where the carbon-based materials are synthesised; transfer means (3, 4, 5) of these metal elements, semiconductors and inorganic compounds thereof to the synthesis chamber; a system to control the temperature of the substrate.

13. An apparatus according to claim 12, wherein this introduction takes place in the form of volatile compounds.

14. An apparatus according to claim 12, wherein this introduction takes place in the form of powders.

15. An apparatus according to claim 14, wherein these powders are
20 elements or compounds.

16. An apparatus according to claim 12, wherein the powders or volatile compounds are contained in a tank (8).

17. An apparatus according to claim 12, wherein these transfer means include a gas flows system which makes it possible to control the density
25 of the powders or vapour present in the gas.

18. An apparatus according to claim 17, wherein this density control takes place by means of controlling the particles in the gaseous flow.

19. An apparatus according to claim 18, wherein this control of the

particles in the gaseous flow is carried out by measuring the concentration of these particles in two areas, separated by a flow measuring and control system, by means of two particle counters, based on laser.

20. An apparatus according to claim 19, wherein these two particle
5 counters are controlled by a computer which operates on the basis of a program which processes the measurement readings to operate the various control valves present.

21. Coatings, films and thin layers made of diamond-based composite materials according to one of the claims 1 - 10.

10 22. A substrate including a coating according to claim 21.

23. A substrate according to claim 22, which is a semiconductor or a conductor.

24. A substrate according to claim 22, which is a heat sink.

25. A cutting instrument including a heat sink according to claim 24.

15 26. Substrates hostile to heterogeneous nucleation of the diamond, including a coating according to claim 21, wherein intermediate composite layers are included, whose metallic concentration gradually diminishes.

27. A method to reduce the substrate/film mismatch and improve adhesion of the diamond film which includes the use of at least one intermediate
20 coating according to claim 21.

28. Use of the materials according to claims 1 - 10, as membranes for sensors, electrodes, transducers.

29. Electric or micro-electronic devices, in discrete, integrated and hybrid form, constituted or including at least one diamond conductive layer
25 according to claims 1 - 10.

30. Use of a device according to claims 28 and 29 in all those situations where bio-compatibility is required.

31. Use of the materials according to claims 1 - 10 for the coating of

metallic prostheses to be implanted into the human body.

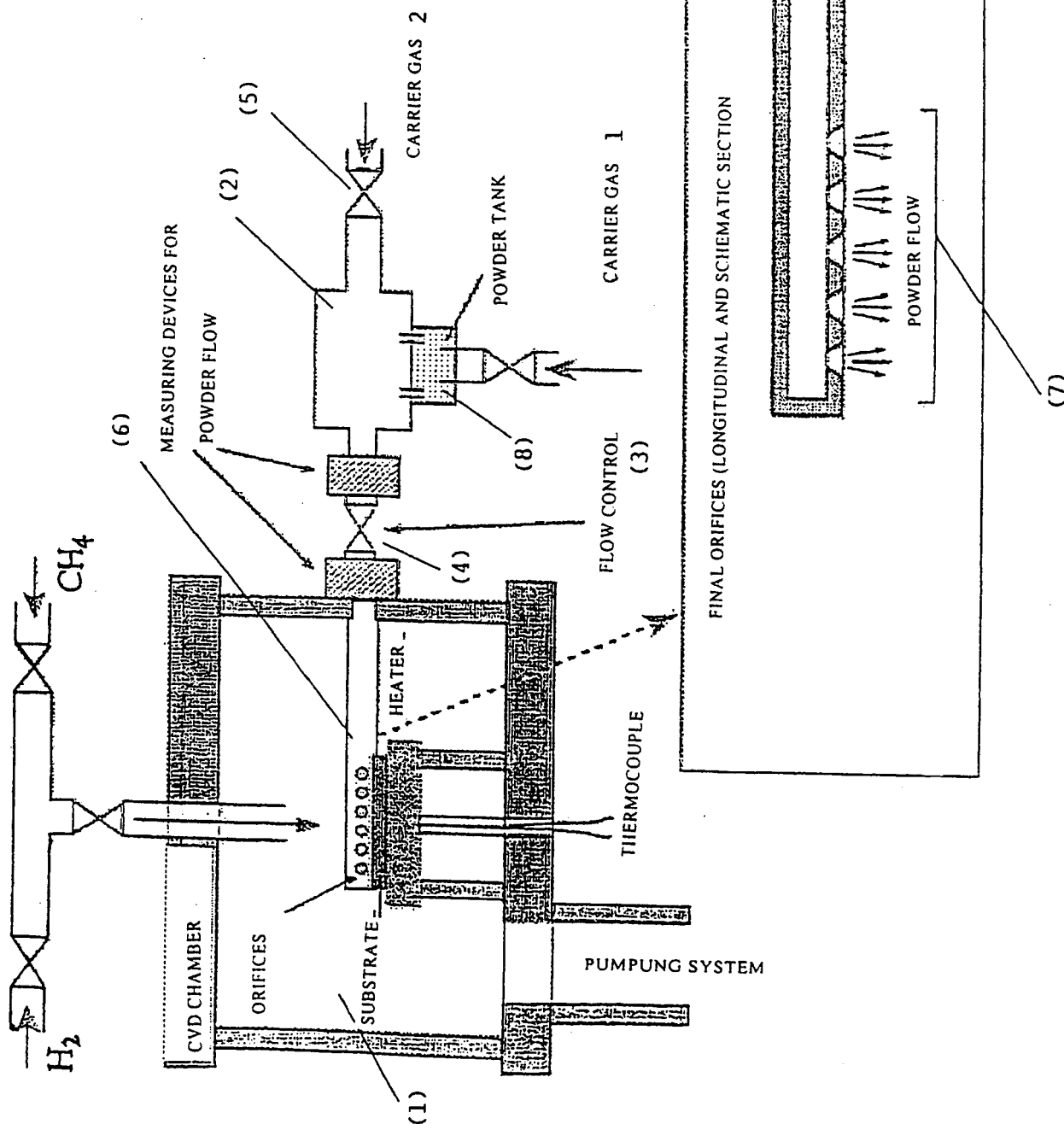
32. Superconductor material including one of the materials according to claims 1 - 10.

33. Mixed layers containing ions which emit (near IR, IR, UV, visible) at
5 room temperature, including at least one of the materials according to
claims 1 - 10.

34. Solid state laser and electro-optical devices including a mixed layer of claims 1 - 10 and 32.

35. Use of the apparatus according to claims 11 - 20 for the synthesis of
10 C_3N_4 .

FIGURE





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<p>(21) International Application Number: PCT/EP99/03547</p> <p>(22) International Filing Date: 24 May 1999 (24.05.99)</p> <p>(30) Priority Data: MI98A001159 26 May 1998 (26.05.98) IT</p> <p>(71) Applicants (for all designated States except US): UNIVERSITA' DEGLI STUDI DI ROMA "TOR VERGATA" [IT/IT]; Dipartimento Di Scienze e Tecnologie Chimiche, Via della Ricerca Scientifica, I-00133 Roma (IT). UNIVERSITA' DEGLI STUDI DI ROMA "LA SAPIENZA" [IT/IT]; Dipartimento Di Energetica, Piazzale Aldo Moro, 05, I-00185 Roma (IT).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): TERRANOVA, Maria, Letizia [IT/IT]; (IT). ROSSI, Marco [IT/IT]; Università degli Studi di Roma "La Sapienza", Via A. Scarpa, 14-16, I-00161 Roma (IT). SESSA, Vito [IT/IT]; (IT). PICCIRILLO, Susanna [IT/IT]; Università di Roma "Tor Vergata", Via della Ricerca Scientifica, I-00133 Roma (IT).</p> <p>(74) Agent: MINOJA, Fabrizio; Bianchetti Bracco Minoja S.r.l., Via Rossini, 8, I-20122 Milano (IT).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> <p>(88) Date of publication of the international search report: 27 April 2000 (27.04.00)</p>
<p>(54) Title: NEW CLASS OF DIAMOND-BASED MATERIALS AND TECHNIQUES FOR THEIR SYNTHESIS</p> <p>(57) Abstract</p> <p>Hereafter are described diamond-based composite materials consisting of sub-micrometric or nanometric dispersions of metallic elements semiconductors and their inorganic compounds in diamond-structured carbon polymorphic matrices together with the techniques and apparatus for their preparation.</p>		

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INTERNATIONAL SEARCH REPORT

International Application No.

PC 99/03547

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C23C16/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 42 10 508 C (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG EV.) 8 April 1993 (1993-04-08)	1,2,5,6, 11, 21-23, 27,29
A	the whole document	3,7-10, 12-20, 28,33,34
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

29 September 1999

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 99/03547

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WEISSMANTEL C ET AL: "Structure property relationships of carbonaceous films grown under ion enhancement"</p> <p>PROCEEDINGS OF THE 13TH INTERNATIONAL CONFERENCE ON METALLURGICAL COATINGS, SAN DIEGO, CA, USA, 7-11 APRIL 1986, vol. 4, no. 6, pages 2892-2899, XP002116947</p> <p>Journal of Vacuum Science & Technology A (Vacuum, Surfaces, and Films), Nov.-Dec. 1986, USA</p> <p>ISSN: 0734-2101</p> <p>page 2892</p> <p>page 2898, "B.i-C/Me composite film"-page 2899</p> <p>---</p>	1-3,6, 21-23
X	<p>US 5 352 493 A (PYPKIN BORIS ET AL)</p> <p>4 October 1994 (1994-10-04)</p> <p>the whole document</p> <p>---</p>	1-3,6, 21-23, 28-31
X	<p>DORFMAN B ET AL: "PHYSICAL PROPERTIES OF DIAMOND-LIKE NANOCOMPOSITE FILMS"</p> <p>MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS,</p> <p>vol. 351, 1 January 1994 (1994-01-01), pages 43-48, XP000602705</p> <p>ISSN: 0272-9172</p> <p>the whole document</p> <p>---</p>	1-3,6, 21-23, 28,29
X	<p>DORFMAN B ET AL: "DIAMOND-LIKE NANOCOMPOSITE COATINGS: NOVEL THIN FILMS"</p> <p>ADVANCES IN SCIENCE AND TECHNOLOGY. NEW DIAMOND AND DIAMOND-LIKE FILMS,</p> <p>vol. 6, 1 January 1995 (1995-01-01), pages 219-226, XP000602720</p> <p>the whole document</p> <p>---</p>	1-3, 21-23, 26,28-33
A	<p>LEE J H ET AL: "MECHANICAL PROPERTIES OF A-C:H AND A-C:H/SIOX NANOCOMPOSITE THIN FILMS PREPARED BY ION-ASSISTED PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION"</p> <p>THIN SOLID FILMS,</p> <p>vol. 280, no. 1/02,</p> <p>1 July 1996 (1996-07-01), pages 204-210, XP000637289</p> <p>ISSN: 0040-6090</p> <p>abstract</p> <p>page 209, "Conclusion"</p> <p>---</p> <p>-/--</p>	1,21,27

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/JP 99/03547

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 97 48836 A (DORFMAN BENJAMIN F) 24 December 1997 (1997-12-24)</p> <p>page 1, line 9 - line 26 page 2898, "B.i-C/Me composite films" - page 2899 page 3, line 34 -page 4, line 21 page 8, line 37 -page 9, line 27 page 12, line 12 - line 16 page 17, line 7 - line 17 examples 1-10</p>	<p>1,2,21, 22,24, 25,28-32</p>
A	<p>--- KLAGES C P ET AL: "MICROSTRUCTURE AND PHYSICAL PROPERTIES OF METAL-CONTAINING HYDROGENATED CARBON FILMS" MATERIALS SCIENCE FORUM, vol. 52/53, 1 January 1989 (1989-01-01), pages 609-644, XP000570912 ISSN: 0255-5476 the whole document -----</p>	<p>1,11,21</p>

International application No.
PCT/EP 99/03547

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

- Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-34

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-34

Claims 1-34: Diamond based composite materials, apparatus for its preparation, coating based on the diamond based composite materials and several uses of the diamond based composite materials

2. Claim : 35

Use of the apparatus for the synthesis of C₃N₄.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/03547

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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